

Photoinitiated RAFT Polymerization in the Presence of Trithiocarbonate

Rong Ran,¹ You Yu,¹ Tao Wan²

¹State Key Laboratory of Polymer Materials Engineering, College of Polymer Science and Engineering, Sichuan University, Chengdu 610065, China

²College of Materials and Chemistry and Chemical Engineering, Chengdu University of Technology, Chengdu 610059, China

Received 26 May 2006; accepted 28 September 2006

DOI 10.1002/app.25581

Published online 27 March 2007 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: A reversible addition–fragmentation chain transfer agent, *S,S'*-bis(α,α' -dimethyl- α'' -acetic acid)trithiocarbonate (TTCA), for free radical polymerization was synthesized. The photopolymerizations (Szwarc et al., *J Am Chem Soc* 1956, 78, 2656) of styrene (St) and butyl acrylate in the presence of TTCA were carried out at room temperature, and the results showed that both $\ln[M]_0/[M]$ and molecular weight were linearly increased with monomer conversion, while the molecular weight distribution became slightly narrower as monomer conversion increased. Moreover, the calculated molecular weight of PSt and PBA agreed quite well with the experiment values determined by gel permeation chromatog-

raphy and NMR. These experimental data demonstrated characteristics of controlled/living photopolymerizations. In addition, the triblock copolymer, PSt-PBA-PSt, with very good control over molecular weight and narrow polydispersity (PDI = 1.12–1.14), was successfully prepared using PSt–S–C(=S)–S–PSt as macrophotoinitiator under UV irradiation at room temperature. Both FTIR and ¹H NMR spectra data indicated the presence of trithiocarbonate structure in PSt. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 398–404, 2007

Key words: trithiocarbonate; living polymerization; photopolymerization; block copolymers; styrene

INTRODUCTION

Since Szwarc et al.¹ first reported the concept of living polymerization in 1956, many living polymerization systems such as anionic polymerization (including group-transfer polymerization), cationic polymerization, and living free radical polymerization have been reported,^{2–8} among which living free radical polymerization has been received much more attention in recent years because of its relatively mild synthetic conditions compared with ionic polymerization. And majority of commercial value polymer products are produced by radical polymerization, and their molecular weight distribution (MWD) are relatively wide, so the investigation of living free radical polymerization has important academic and practical value. A variety of polymers can be produced under mild conditions with well-defined structures and narrow MWD.^{6–8} Currently, the main techniques used to achieve living behavior are nitroxide-mediated polymerization,^{9–13} atom transfer radical polymerization,^{14–18} and reversible addition–fragmentation chain transfer (RAFT) process.^{19–22}

Recently intensive studies have been carried out using RAFT technique for the controlled/living radi-

cal polymerization because of its numerous monomers available under various conditions since its discovery in 1998.^{19–22} The most common chain transfer agents (CTA), which mediate the growing chain radicals via an equilibrium of radical intermediates, are dithioester^{23,24} and trithiocarbonate,^{23,25–27} and the latter has been attracted much attention because of its ease of synthesis and purification. Up to now trithiocarbonate has been proven to be especially useful for the controlled polymerization of styrene (St), acrylate, acrylamide monomers, and their derivatives under extremely facile conditions.²⁸

The initiation methods of RAFT process usually have three types: thermoinitiation,^{20–27} UV-initiation,^{29,30} and γ -radiations initiation.^{31–33} Compared with the time-consuming thermal initiation processes, the photoinitiated free radical polymerization is extremely fast. Besides, the reaction at ambient temperature makes the process easy to set up and the energy cost is significantly reduced. One of the earliest attempts to control molecular weight (MW) and end functional groups of the resulting polymers by a photoinitiated free radical chemistry is the sulfur iniferter process introduced by Otsu and coworkers.^{34–39} Under UV irradiation, considerable amount of the light is absorbed by the iniferter leading to generate a carbon-centered radical and a sulfur-centered radical. However, the sulfur-centered radical is not stable enough to monomer and can initiate polymerization.

Correspondence to: R. Ran (ranrongsong@sina.com).

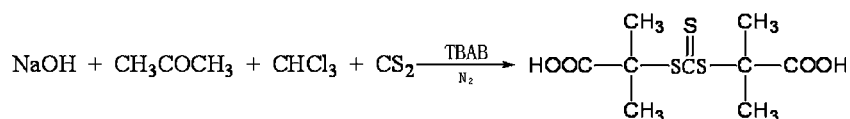


Figure 1 Synthesis of RAFT reagent TTCA.

As a result, the polymers obtained by the iniferter approach were found to have polydispersities similar to those from conventional free radical processes. Other photoinitiated polymerizations of RAFT have also been studied by Quinn et al.,²⁹ You et al.,³⁰ and Lu et al.⁴⁰ In their work, 1-phenylethyl phenyldithioacetate, dibenzyl trithiocarbonate, *S*-dodecyl-*S'*-(α,α' -dimethyl- α'' -acetic acid) trithiocarbonate and cumyldithiobenzoate were used as CTA, respectively.

In spite of promising early studies^{29,30,34–40} reported, there is no report of controllable polymerization with defined structure and narrow molecular distribution synthesized by RAFT under UV irradiation at room temperature, especially using *S,S'*-bis(α,α' -dimethyl- α'' -acetic acid) trithiocarbonate (TTCA) as CTA. In this article, we present the living/controlled photopolymerizations of St and butyl acrylate (BA) in the presence of TTCA with controlled MW and MWD for the first time. The structures of the PSt with trithiocarbonate group are confirmed by FTIR and ¹H NMR spectra. In addition, PSt-PBA-PSt triblock copolymers were successfully synthesized by UV-induced RAFT process with controlled MW and narrow MWD. To our best knowledge, such block copolymers have not been produced by RAFT photopolymerization techniques so far.

EXPERIMENTAL

Materials

Styrene, methyl methacrylate, and *n*-butyl acrylate (BA) (Shanghai Chemical, AR) were passed through a column of activated basic alumina (50–200 μm) to remove the inhibitor. Tetrahydrofuran (THF), carbon disulfide were analytical grade and used after purification. Tetrabutyl bromize ammonium, sodium hydroxide, chloroform, and acetone (Shanghai Chemical AR) were used as received.

Synthesis of *S,S'*-bis(α,α' -dimethyl- α'' -acetic acid) trithiocarbonate

The structure of TTCA is shown in Figure 1 and was prepared according to Ref. 27. Carbon disulfide (2.74 g, 36 mmol), chloroform (10.75 g, 90 mmol), acetone (5.23 g, 90 mmol), and tetrabutyl bromize ammonium (0.229 g, 0.71 mmol) were mixed with 12 mL of mineral spirits in a 1-L jacketed reactor cooled with tap water under nitrogen. Sodium hydroxide

(50%) (20.16 g, 0.252 mol) was added drop-wise over 90 min to keep the temperature below 25°C, and the reaction was stirred overnight. About 90 mL of water was then added to dissolve the solid, followed by addition of 12 mL concentrated HCl (*caution! gas, mercaptan odor*) to acidify the aqueous layer. Stir for 30 min with nitrogen purge. Filter and rinse the solid thoroughly with water. Dry to constant weight to collect a yellow product. After recrystallization in ethanol, the yellow product was gained (yield: 62.1%). (mp: 172–175°C). ¹H NMR (δ): 8.01 (s(wide), —COOH), 1.67 (s, 12H, —CH₃); IR (KBr): $\nu_{(\text{O}-\text{H})}$ 3426.66 cm^{-1} , $\nu_{(\text{C}-\text{H})}$ 2955.71, 2918.17, 2851.09 cm^{-1} , $\nu_{(\text{C}=\text{O})}$ 1700.59 cm^{-1} , $\delta_{(\text{C}-\text{H})}$ 1468.83 cm^{-1} , $\nu_{(\text{C}-\text{S}-\text{C})}$ 1286.45 cm^{-1} , $\nu_{(\text{C}=\text{S})}$ 1063.80 cm^{-1} .

Photopolymerization in the presence of TTCA

Black lamps, with peak emissions at 365, 402, 430 nm and the emission at 365 nm being maximum, were used as a UV radiation source. UV-vis spectroscopy studies indicated that TTCA shows undesirable strong absorption at 365 nm, matches the UV radiation (see Fig. 2). The photopolymerization was carried out in a 5-mL ampoule. The ampoule was filled with 2.0 mL of monomer and 10 mg (17.6 mM) of TTCA, and then flame-sealed after being bubbled with N₂ for 10 min to eliminate oxygen, followed by UV irradiation at room temperature, with 18-W four black lamps as light source. After a predetermined

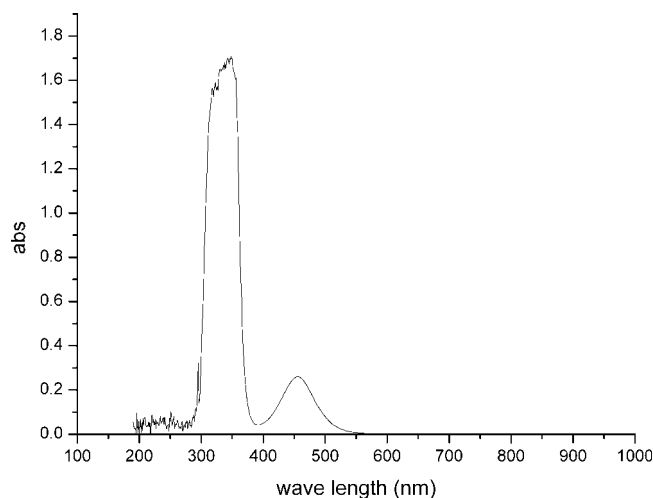


Figure 2 UV spectra of RAFT reagent TTCA dissolved in benzene.

TABLE I
Photopolymerization of MMA, BA, and St in the Presence of TTCA

No.	Monomer	[TTCA] mmol/L	Time (h)	Conversion %	\overline{M}_n th ^a	\overline{M}_n GPC ^b	$\overline{M}_w/\overline{M}_n$ ^b
1	BA	17.6	20	19.8	12,570	10,840	1.13
2	BA	17.6	48	77.72	44,429	37,730	1.05
3	St	17.6	28	5.5	3,410	3,880	1.14
4	St	17.6	67	21.7	12,620	12,100	1.14
5	St	17.6	72	25.1	12,620	15,600	1.12

Reaction conditions: room temperature; the distance from lamp to sample was 40 cm.

^a Calculated according to eq. (1): \overline{M}_n th = Conv × (W/n) + M_{TTCA} .

^b \overline{M}_n GPC and $\overline{M}_w/\overline{M}_n$ were obtained by gel permeation chromatography, compared with standard PSt.

time, the ampoule was opened, and the reaction mixture was diluted with THF. The polymer was precipitated in a 10-fold excess of methanol (or ethanol), recovered by filtration, and finally dried at 55°C under vacuum up to constant weight. Conversions were determined gravimetrically.

Synthesis of triblock copolymers

Triblock copolymers were synthesized by solution RAFT polymerization. A similar procedure was performed as described in Photopolymerization in the Presence of TTCA except TTC. The polymer obtained in this section was used as macro RAFT agent.

Characterizations of polymers

The MW M_n and the MWD were measured on a Agilent 1100 gel permeation chromatography (GPC) equipped with Pl gel column, monodisperse PSt as standard, with THF (1.0 mL min⁻¹) as eluent. Infrared spectra were recorded on a Nicolet 560 spectrometer. ¹H NMR spectra were analyzed on a Varian Unity Inova 400 instrument with CDCl₃ as solvent and tetramethylsilane as internal standard. Melting point of trithiocarbonate (TTCA) was measured on a X4 Melting Point Microscope Instrument. UV spectra of RAFT reagent (TTCA) was measured by UV-vis spectrometer.

RESULTS AND DISCUSSION

Photopolymerization with TTCA

The photopolymerizations of St, methyl methacrylate, and BA with TTCA without the addition of any thermal or photo initiator were performed by UV irradiation at different time intervals. The MW and polydispersity values determined by GPC traces are shown in Table I and Figures 3 and 4 versus global conversion. The M_n values of PBA increased linearly until about 78% conversion, to reach 3.8×10^4 g mol⁻¹, with $M_w/M_n = 1.05$. These values are in agreement

with the predicted MWs. Moreover, PSt RAFT photopolymerization were carried out under the same conditions, it was possible to reach 1.6×10^4 g mol⁻¹, with $M_w/M_n = 1.12$ (25% conversion). Besides, kinetic curves of PSt and PBA photopolymerization, as shown in Figures 3 and 4, demonstrated the linear evolution of the number-average MW with conver-

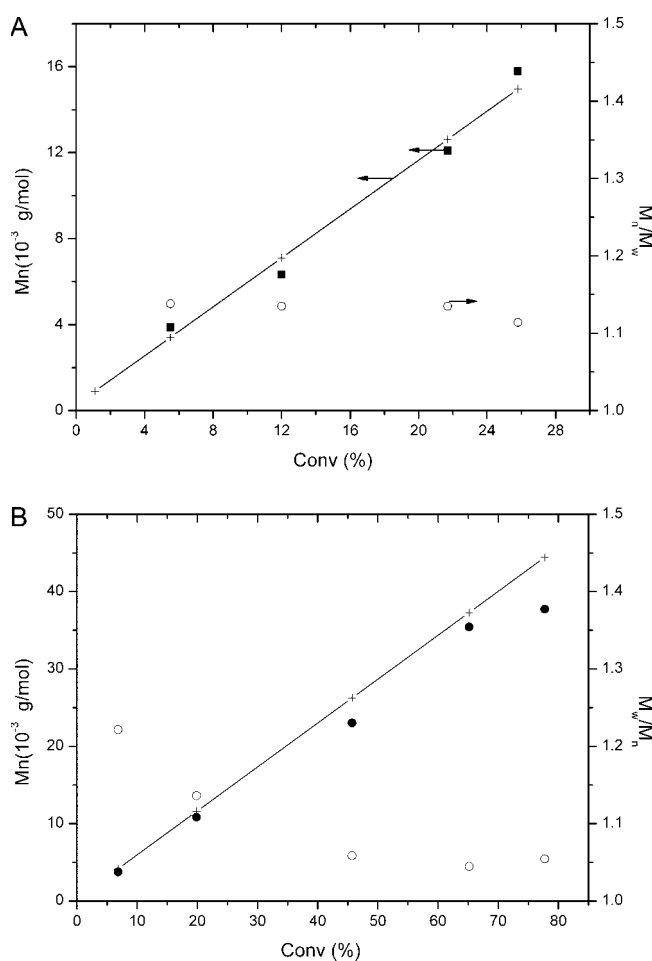


Figure 3 Dependence of molecular weight and molecular weight distribution on monomer conversion for St (a) and BA (b) photopolymerization in the presence of TTCA (■) \overline{M}_n GPC, (○) $\overline{M}_w/\overline{M}_n$, (+) \overline{M}_n th.

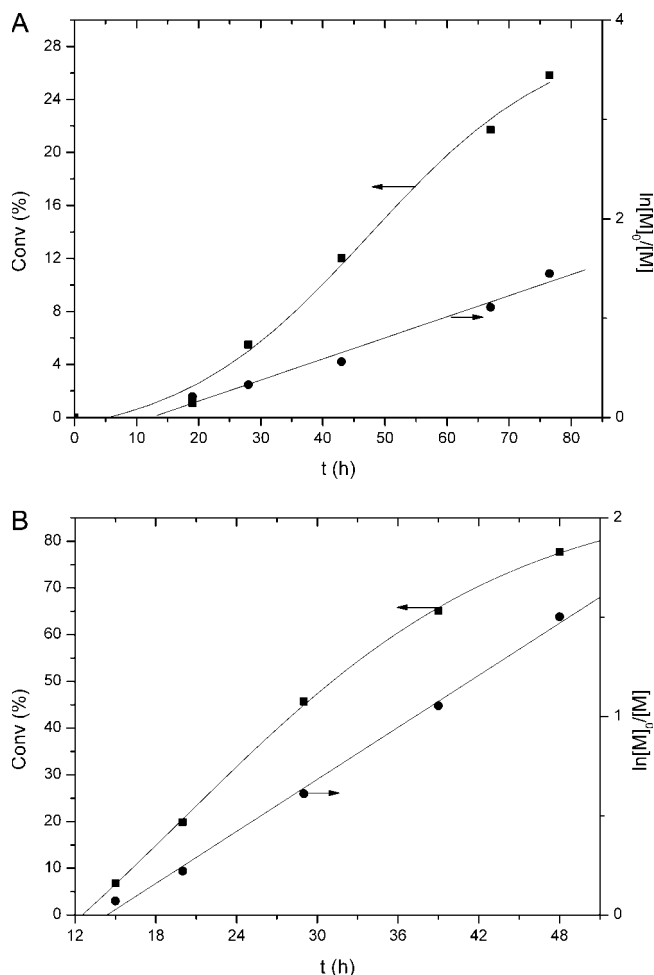


Figure 4 Dependence of monomer conversion and $\ln[M]_0/[M]$ on polymerization time for St (a) and BA (b) photopolymerization in the presence of TTCA.

sion, and the MWD of PSt and PBA became slightly narrower as monomer conversion increased. These results were entirely consistent with controlled/

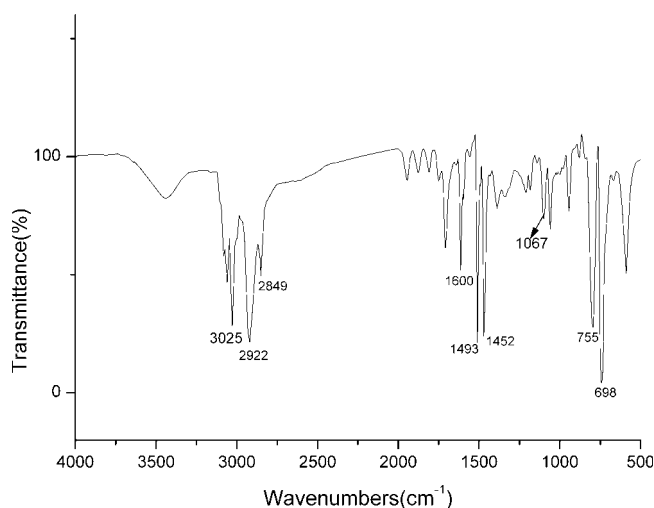


Figure 5 FTIR spectra of PSt prepared by photopolymerization in the presence of TTCA.

“living” polymerizations. In the photopolymerizations, pseudo first-order kinetics were confirmed for TTCA mediated photopolymerization of St, BA because of the linear increase of $\ln[M]_0/[M]$ with time (see Fig. 4), confirming that the concentration of radical species remained constant up to about 80% conversion (PBA). The results again suggested the living characteristics photopolymerization behavior of St and BA in the presence of TTCA. TTCA is highly efficient chain-transfer RAFT agent for St and BA under UV radiation, owing to the carboxyl-stabilized tertiary carbon radical produced by the homolysis of carbon–sulfur single bond during polymerization. Although it is too dormant to initiate polymerization, it can reversibly scavenge the propagating radical to form a dormant polymer chain, and irreversible termination reactions between the various radical species, such as primary radicals, and the intermediate RAFT radicals can be restrained. The theoretical molecule weight $M_{n(\text{th})}$, could be calculated according to

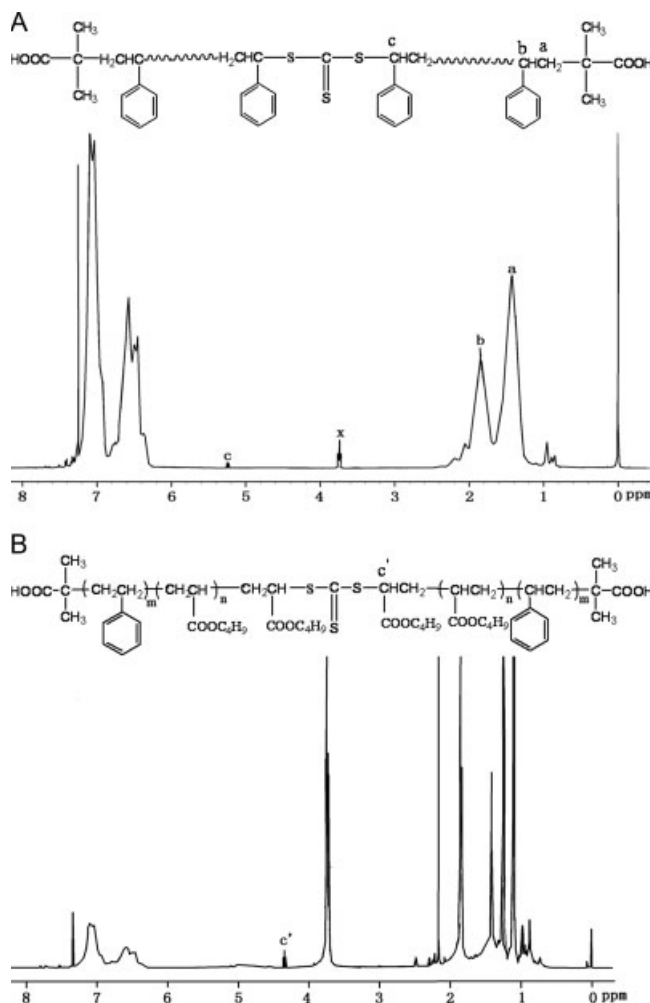


Figure 6 ^1H NMR spectra: (a) PSt–S–C(=S)–S–PSt of PSt TTCA as photoinitiator $X = \text{CH}_3\text{CH}_2\text{OH}$; (b) block copolymer, PSt–PBA–PSt.

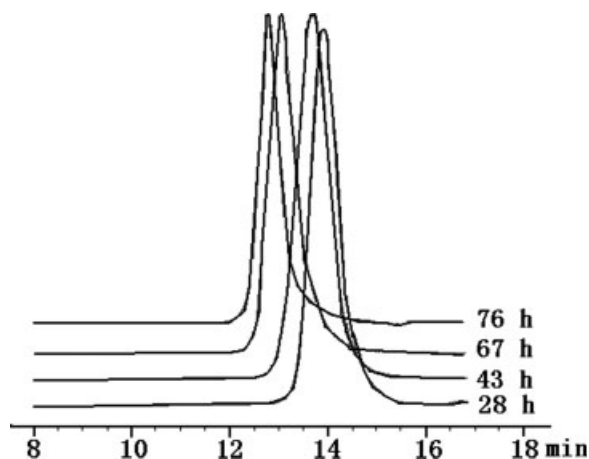


Figure 7 GPC traces for polystyrene formed by photopolymerization of styrene (bulk) with TTCA 0.076M for 28, 43, 67, 76 h.

$$\overline{M}_{th} = Conv \times (W/n) + M_{TTCA} \quad (1)$$

where W is the initial monomer weight, n is the moles of active centers, and M_{TTCA} is the molecule weight of TTCA, $Conv$ is monomer conversion. Supposing that all TTCA molecules participated in the initiation process and no other side reactions occurred, the number of active centers remained constant throughout the photopolymerization; therefore, the moles of active centers could be determined by moles of TTCA added. The molecule weights $M_{n(th)}$ calculated according to formula (1) are listed in Table I. The MWs of PSt and PBA obtained from GPC agree well with the theoretical MWs [$M_{n(th)}$] as shown in Figure 4, indicating that the MWs of PSt and PBA can be well controlled by the ratio of monomer consumed to TTCA.

Structural analysis

The structure of PSt was characterized by FTIR and 1H NMR. The IR spectra of the PSt prepared by using TTCA as photoinitiator is shown in Figure 5. The IR spectrum of the PSt showed weak absorption at 1067 cm^{-1} , which can be ascribed to the C=S group of

trithiocarbonate. We can also find the absorption peaks of benzene ring at $\nu = 3025, 2922, 2849, 1600, 1493, 1452, 755, \text{ and } 698\text{ cm}^{-1}$. Besides, in the 1H NMR spectrum of a PSt (Fig. 6), the peaks at $\delta = 7.2\text{ ppm}$ correspond to the aromatic protons of the St unit, and the small peaks at $\delta = 5.2\text{ ppm}$ to the methine proton of the St unit next to sulfur. The results of 1H NMR spectrum are also indicative of the presence of the trithiocarbonate groups in the polymers obtained. Provided that each macromolecule contains only one trithiocarbonate group, the number average MW $\overline{M}_{n,NMR}$ can be calculated according to eq. (2).

$$\overline{M}_{n,NMR} = 2 \times [(I_{7.2}/5I_{5.2}) \times 104] + 284 \quad (2)$$

where $I_{7.2}$ and $I_{5.2}$ are the integration values of the peaks at $\delta = 7.2$ and 5.2 ppm , respectively; 104 and 284 are the MWs of St and TTCA, respectively. The result calculated by eq. (2) is $\overline{M}_{n,NMR} = 1.63 \times 10^4$ approaching the value measured by GPC ($\overline{M}_n = 1.58 \times 10^4$).

Figure 7 shows the experimentally determined MW distributions with conversion increasing for a polystyrene (PSt) homopolymer. It is qualitatively clear that the photopolymerization proceeds in a controlled manner with the observed polymer peaks shifting to lower retention times and polydispersities keeping narrow (1.12–1.14) with conversion increasing. Importantly, there is no evidence in the chromatograms of high MW impurity, which can be indicative of termination products. This may preclude the existence of termination products and imply that irreversible termination and side reaction can be negligible.

Synthesis of block copolymer using PSt–S–C(=S)–S–PSt as macrophotoinitiator

The “living” characteristics of the RAFT photopolymerization was further confirmed by the quantitative block copolymer. The last PSt sample of experiment seven in Table I (25.1% conversion, $M_n = 1.6 \times 10^4\text{ g mol}^{-1}$, $M_w/M_n = 1.12$) was used as macro CTA in the RAFT photopolymerization of PBA (as shown in Table II). The corresponding samples have monomodal GPC traces (Fig. 8). The shift of the peaks away

TABLE II
Results of Block Copolymers Prepared by Using the Macrophotoinitiator, PSt–S–C(=S)–S–PSt (No. 7 in Table 1) under UV Irradiation

No.	Monomer/g	Macroinitiators	Conv ^a /%	M_{th} ^b	\overline{M}_n GPC ^c	$\overline{M}_w/\overline{M}_n$ ^d
1	BA(5)	0.2 g (0.0128 mmol)	30.4	130,000	121,000	1.15
2	BA(5)	0.2 g (0.0128 mmol)	47.5	201,000	196,000	1.16
3	BA(5)	0.2 g (0.01284 mmol)	62.1	258,000	210,000	1.15

^a Conversion was determined by determined gravimetrically.

^b Calculated according to eq. (3). $\overline{M}_{th} = Conv \times (W/n) + M_{macroinitiators}$.

^c \overline{M}_n GPC and MWD were obtained by gel permeation chromatography.

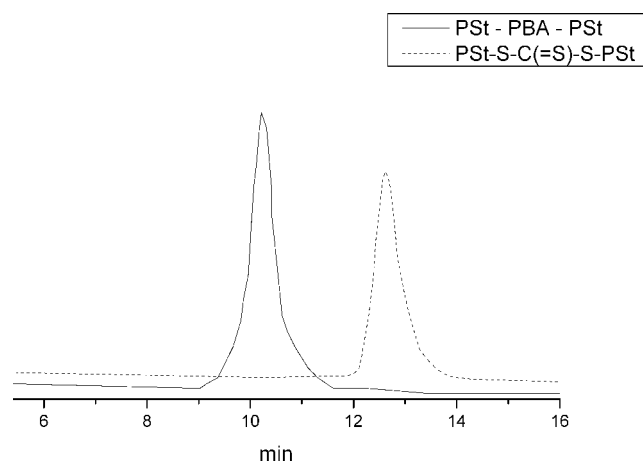


Figure 8 GPC traces for the PSt-based macro-CTA (M_n 15,600, M_w/M_n 1.12) and the corresponding "triblock copolymer" (M_n 210,000, M_w/M_n 1.15).

from the peak of PSt confirms the successful formation of a PSt-PBA-PSt block copolymer. Moreover, there is no clear evidence of low MW impurity because of unreactivated PSt macro-CTA as well as higher MW, presumably because of radical-radical coupling reactions and disproportionation of the intermediate radical, and the experimentally determined M_n agrees very well with the theoretical M_n with the final polydispersity ($M_w/M_n = 1.15$ – 1.16) keeping rather narrow. Another evidence for the formation of triblock copolymers PSt-PBA-PSt is their ^1H NMR spectra shown in Figure 5(b). The peak at $\delta = 5.2$ ppm in Figure 5(a) is completely absent from Figure 5(b), and a new peak at $\delta = 4.4$ ppm, corresponding to the methine proton of the BA unit next to sulfur appears in Figure 5(b). This indicated that this reversible and equally valid strategy led to a better controlled block copolymer with defined structures.

CONCLUSIONS

A RAFT agent, *S,S'*-bis(α,α' -dimethyl- α'' -acetic acid)-trithiocarbonate (TTCA) was successfully synthesized. In the photopolymerizations, the observed linear relationship in the pseudofirst order rate plot for TTCA mediated photopolymerization of St, BA, in conjunction with the linear increase of M_n versus conversion, likewise confirms the living characteristics. The MWs of PSt and PBA obtained from GPC agree well with the theoretical MWs [$M_{n(\text{th})}$], indicating that the MWs of PSt and PBA can be well controlled by the ratio of monomer consumed to TTCA. The measured polydispersity indices M_w/M_n are very low and decrease with conversion. Again, this is characteristic of a controlled/living polymerization. In addition, the triblock copolymer PSt-PBA-

S-C(=S)-S-PBA-PSt were obtained by a two-step process. First, a polystyrene homopolymer was prepared by RAFT. Then, it was used as macro CTA to polymerize the second block. On the GPC traces of the triblock copolymer, the peaks were regularly shifted toward higher MWs and polydispersities keeping narrow (1.12–1.14) as conversion increased, showing a very good control of MWs for block copolymers of different microstructures.

References

1. Szwarc, M.; Levy, M.; Milkovich, R. *J Am Chem Soc* 1956, 78, 2656.
2. Quirk, R. P.; Lynch, T. *Macromolecules* 1993, 26, 1206.
3. Fréchet, J. M. J. *Science* 1994, 263, 1710.
4. Sogah, D. Y.; Hertler, W. R. O.; Webster, W.; Cohen, G. M. *Macromolecules* 1987, 20, 1473.
5. Gorman, C. B.; Ginsburg, E. J.; Grubbs, R. H. *J Am Chem Soc* 1993, 115, 1397.
6. Johnson, C. H. L.; Moad, G.; Solomon, D. H.; Spurling, T.; Vearing, D. J. *Aust J Chem* 1990, 43, 1215.
7. Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. *Trends Polym Sci* 1994, 2, 66.
8. Sawamoto, M.; Kamigaito, M. *Trends Polym Sci* 1996, 4, 183.
9. Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. *Macromolecules* 1993, 26, 2987.
10. Keoshkerian, B.; Georges, M. K.; Boils-Boissier, D. *Macromolecules* 1995, 28, 6381.
11. Keoshkerian, B.; Georges, M. K.; Quinlan, M.; Veregin, R. P. N.; Goodbroad, B. *Macromolecules* 1998, 31, 7559.
12. Fukuda, T.; Terauchi, T.; Goto, A.; Tsujii, Y.; Miyamoto, T. *Macromolecules* 1996, 29, 3050.
13. Schmidt-Naake, G.; Butz, S. *Macromol Rapid Commun* 1996, 17, 661.
14. Wang, J. S.; Matyjaszewski, K. *Macromolecules* 1995, 28, 7901.
15. Percec, V.; Kim, H. J.; Barboiu, B. *Macromolecules* 1997, 30, 6702.
16. Sawamoto, M.; Kanigaito, M. *Trends Polym Sci* 1996, 4, 371.
17. Pan, C. Y.; Lou, X. D.; Wang, Y. L.; Wu, C. P. *Acta Polym Sin* 1998, 3, 311.
18. Matyjaszewski, K.; Coca, S.; Nakagawa, Y.; Xia, J. *Polym Mater Sci Eng* 1997, 76, 147.
19. Chiefari, J.; Chong, Y. K. B.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T. P. T.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, C. L.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* 1998, 31, 5559.
20. Chong, Y. K. B.; Le, T. P. T.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* 1999, 32, 2071.
21. Chiefari, J.; Mayadunne, R. T. A.; Moad, G.; Thang, S. H. *Polym Prepr (Am Chem Soc Div Polym Chem)* 1999, 2, 342.
22. Mayadunne, R. T. A.; Rizzardo, E.; Chiefari, J.; Krstina, J.; Moad, G.; Postma, A.; Thang, S. H. *Macromolecules* 2000, 33, 243.
23. Chong, Y. K.; Krstina, J.; Le, T. P. T.; Moad, G.; Postma, A.; Rizzardo, E.; Thang, S. H. *Macromolecules* 2003, 36, 2256.
24. Chiefari, J.; Mayadunne, R. T. A.; Moad, C. L.; Moad, G.; Rizzardo, E.; Postma, A.; Skidmore, M. A.; Thang, S. H. *Macromolecules* 2003, 36, 2273.
25. Rizzardo, E.; Chiefari, J.; Moad, G.; Mayadunne, R. T. A.; Thang, S. H. *Polym Prepr* 1999, 40, 342.
26. Hong, J.; Wang, Q.; Lin, Y. Z.; Fan, Z. Q. *Macromolecules* 2005, 38, 2691.
27. Lai, J.; Filla, T. D.; Shea, R. *Macromolecules* 2002, 35, 6754.
28. Liu, J.; Hong, C. Y.; Pan, C. Y. *Polymer* 2004, 45, 4413.

29. Quinn, J. F.; Barner, L.; Barner-kowollik, C. *Macromolecules* 2002, 35, 7620.
30. You, Y. Z.; Hong, C. Y.; Bai, R. K.; Pan, C. Y.; Wang, J. *Macromol Chem Phys* 2002, 203, 477.
31. Barner, L.; Quinn, J. F.; Barner-Kowollik, C.; Vana, P.; Davis, T. P. *Eur Polym Mater* 2003, 39, 449.
32. Quinn, J. F.; Barner, L.; Rizzardo, E.; Davis, T. P. *J Polym Sci Part A: Polym Chem* 2002, 40, 19.
33. Hong, C. Y.; You, Y. Z.; Bai, R. K.; Pan, C. Y.; Borjian, G. *J Polym Sci Part A: Polym Chem* 2001, 39, 3934.
34. Otsu, T.; Matsunaga, T.; Kuriyama, A.; Yoshioka, M. *Eur Polym Mater* 1989, 25, 643.
35. Otsu, T.; Yoshioka, M.; Tanaka, T. *Eur Polym Mater* 1992, 28, 1325.
36. Doi, T.; Matsumoto, A.; Otsu, T. *J Polym Sci Part A: Polym Chem* 1994, 32, 2911.
37. Otsu, T.; Yoshioka, M. *Makromol Chem Rapid Commun* 1982, 12, 77.
38. Otsu, T.; Yoshioka, M.; Kuriyama, A. *Polym Bull (Berlin)* 1982, 7, 45.
39. Otsu, T.; Kuriyama, A.; Yoshioka, M. *Kobunshi Ronbunshu* 1983, 40, 585.
40. Lu, L. C.; Yang, N. F.; Cai, Y. L. *Chem Commun* 2005, 5287.
41. Wang, R.; Charles, L. M.; Andrew, B. L. *Macromolecules* 2005, 38, 9518.